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Grafting of 2-Hydroxypropyl Methacrylate onto Poly(ethylene terephthalate) Fibers and Dye Ability

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In this study, dye ability of the poly(ethylene terephthalate) fibers after grafting with 2-hydroxypropyl methacrylate is reported using Disperse Red S-BFW as disperse dye. Results of the dye ability showed that by increasing of the percentage of grafted fibers, their dye ability increases to 21.21 %-grafted product and then decreases. The effect of 0.5 % emulsifier (anionic, cationic and nonionic) on fibers dye ability was investigated. While at the presence of cetyltrimethyl ammonium bromide no dye ability could be observed, in dyeing of uncopolymerized fibers, the effect of hexadecyl poly[oxyethylene(30)] alcohol (OC-30) was more than sodium lauryl sulphate and cetyltrimethyl ammonium bromide. But in graft product with the increase of the graft product, sodium lauryl sulphate, cetyltrimethyl ammonium bromide and OC-30 showed more dye ability effect on the fibers, respectively. On the other hand, with the use mixture initiators including benzoyl peroxide (Bz_2O_2), 4-4'-azo*bis*(4-cyanovaleric acid) (ACV) an intensifying effect on the graft product was observed and the copolymerization time at the presence of (Bz_2O_2/ACV = 1/3) decreased. The characterization of graft fibers with thermogravimetric analysis, scanning electron microscopy and Fourier transform infrared methods have been investigated.

Key Words: Poly(ethylene terephthalate), 2-Hydroxypropyl methacrylate, 4-4'-Azo*bis*(4-cyanovaleric acid), Benzoyl peroxide.

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers have a salient place among synthetic fibers. Poly(ethylene terephthalate) fibers do not contain chemically reactive groups and their structure is highly crystalline. Hence, these materials can not combine with the cationic, anionic, acidic and basic dyes. So, the dye ability of PET fibers accomplish with the use of disperse dyes. Many researchers have been investigated the dye ability of PET fibers after grafting by different monomers onto PET[1-11]. Vinyl monomers can be grafted onto PET fibers under the influence of free-radical initiators and improved their dye ability with reactive dyes[5-9]. The aim of this study is to determine the effect of different emulsifiers such as sodium lauryl sulphate (SLS), cetyltrimethyl ammonium bromide (CTAB) and hexadecyl poly[oxyethylene(30)] alcohol (OC-30) on the dye ability with disperse Red S-BFW as a disperse dye. On the other hand, characterization of the grafted fibers were investigated by thermogravimetric analysis, Fourier transform infrared and scanning electron microscopy.

In our previous work optimum grafting conditions were ascertained: [ACV] = 4.0×10^{-3} M, [2-HPMA] = 0.5 M, temperature = 75 ºC, time = 1 h (in press). In this article effect of the mixture of initiators (Bz_2O_2-ACV) at the yield of grafting was compared with the using of individual of them.

EXPERIMENTAL

2-Hydroxypropyl methacrylate (2-HPMA) as monomer was supplied by Merck (Germany). Poly(ethylene terephthalate) (PET) fibers (44 filaments, 167 dtex) were used in all experiments. 4,4'-Azo*bis*(4-cyanovaleric acid) (ACV) and benzoyl peroxide (Bz_2O_2) obtained from Aldrich (England). All emulsifiers and solvents such as SLS, CTAB, OC-30, N,N-dimethylformamide (DMF), toluene, acetone, methanol and chloroform were analytical of grade and supplied by Merck. Doubly distilled water has been used in all experiments. Poly(ethylene terephthalate) samples were prepared as small hank (0.3 ± 0.001 g) Soxhlet-extracted for 6 h with acetone and dried at ambient temperature. 2-Hydroxypropyl methacrylate has been used after distilled under reduced pressure in inert atmosphere (23 mmHg, T_{BP} = 99 ºC). 4,4'-Azo*bis*(4-cyanovaleric acid) and benzoyl peroxide after purification have been used in experiments. 4,4'-Azo*bis*(4-cyanovaleric acid) was suspended in doubly distilled water, then the solid sodium bicarbonate was added and acidified with the use of 1 M HCl. Finally, the solid was filtered and washed with ice cold water and dried at the room temperature in vacuum. Benzoyl peroxide was recrystallized twice from the methanol-chloroform mixture and dried in vacuum. Disperse dye, emulsifiers and solvents have been used without further purification.

Grafting procedure: The PET fiber specimen was placed in a 100 mL Pyrex tube possessing the required concentration of monomer and initiator in 5 mL acetone. Then the volume of the mixture was immediately placed into a water bath at the fixed polymerization temperature. After desirable time, the fiber sample was taken out of the tube and for washing of undesirable homopolymers, Soxhlet-extracted with N,N-dimethylformamide and mixture of (toluene-acetone) (50 % vol. acetone) for 6 and 8 h, respectively. Finally, the sample was dried in vacuum at 50 ºC. Per cent graft yield was calculated from the increase in the weight of the original PET after grafting[11].

$$G(\%) = \frac{(W_g - W_o)}{W_o} \times 100$$

In this equation, W_g and W_o denote the weights of the grafted and original PET, respectively.

Dyeing procedure: Dye ability of fibers was investigated by the use of disperse Red S-BFW in the absence and presence of 0.5 % emulsifier. So, calibration curve for the concentration range 1.6×10^{-2}-8.0×10^{-2} g dye/L in a mixture of acetone and toluene (30 % vol. acetone) was drawn by the use of Shimadzu. UV-1601-PC spectrophotometer in λ_{max} (505 nm). The amount of 0.075 g of fiber was placed in the tube and then 4×10^{-3} g of dye and 50 mL of distilled water was added to the tube. The tube was placed in a water bath in 85 ºC for 2 h. After that the washing fiber with hot water carefully and the absorbed dye was extracted with 50 mL of solvents (toluene-acetone) at 50 ºC. At the end, the amount of extracted dye was measured by the spectrophotometer in λ_{max}.

Characterization methods: The FTIR spectra of 2-HPMA grafted PET fibers were recorded using a Bruker Equinox FTIR spectrophotometer with KBr discs. The SEM micrographs of PET fibers, coated with gold, were achieved using a Philips XL 30 scanning electron microscope. Thermogravimetric analysis of the PET fibers carried out with TGA V5.1A Dupont in helium atmosphere at the flow rate of 200 mL/min between (25-700 ºC) at a heating rate of 10 ºC/min.

RESULTS AND DISCUSSION

Characterization of the fibers: FTIR spectrum was recorded for 2-HPMA grafted PET fiber (Fig. 1). The absorptions at 1091 and 1712 cm^{-1} correspond to the (C-O) stretching vibration of the secondary alcohol and stretching vibration of the (C=O),

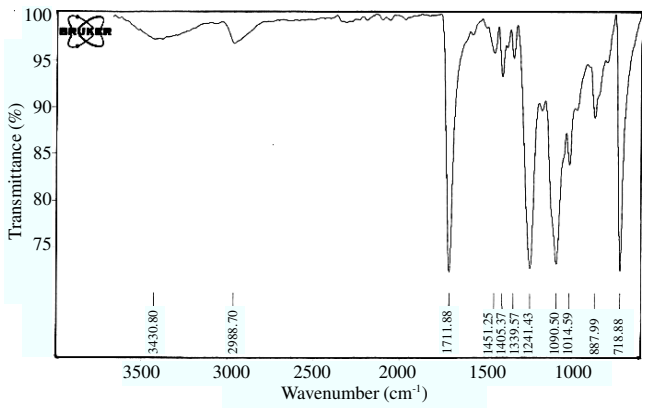
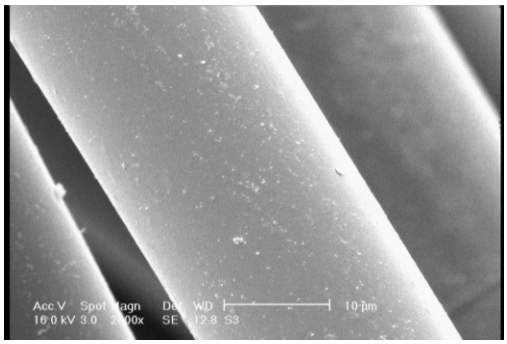
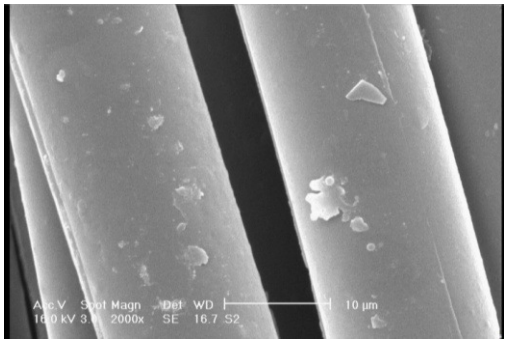


Fig. 1. FTIR spectrum of 2-HPMA grafted PET fiber

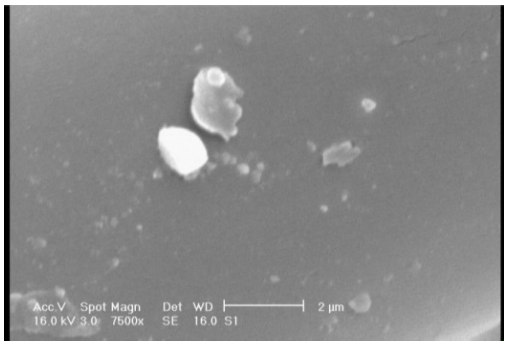
respectively. These absorption peaks showed that the monomer has been grafted to PET fiber. The effect of 2-HPMA grafting upon the surface morphology of PET fibers are showed in Fig. 2. As shown in micrographs, by increasing the yield of grafting, the fibers showed a heterogeneous structure and the surface of them were very rough[7,11] [Fig. 2(a-c)]. The thermogravimetric analysis results revealed that the decomposition temperature of the fibers decreased with the grafting[11-13]. Thermal decomposition temperature of 49.0 % of the grafted to PET fiber decreased to 245 ºC. So, by comparing the thermograms shown in Fig. 3(a-c) with each other, it is concluded that by increasing the percentage of the grafted fibers, the thermal stability decreases. The results of these three methods emphasize the grafting of 2-HPMA onto PET chains.



(a)



(b)



(c)

Fig. 2. SEM micrographs of (a) 12.5 % (2000x), (b) 49.0 % grafted (2000x) and (c) 49.0 % (7500x)

Effect of mixture of initiators: The graft copolymerization has been done with the use of individual and mixture of initiators (Bz_2O_2) and (ACV) at fixed condition: [M] = 0.5 M, T = 75 ºC, t = 1 h. Results showed that the use of mixture

of initiators increased the grafting yield (71.42 %). While, maximum grafting was recorded for ACV and Bz_2O_2, 52.55 and 45.70 %, respectively. This effect has an important role in textile industry and the time of reaction can be decreased by the use of mixture of free radical initiators (Figs. 4-7). Hence, with two initiators concurrently, with different decomposition temperatures, synthesis time would decrease.

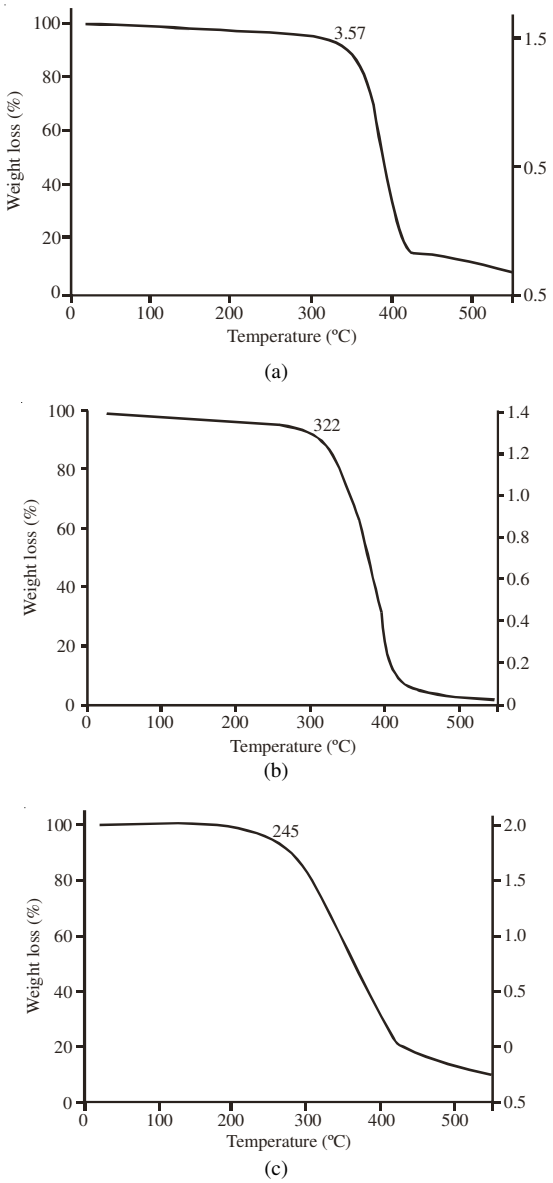


Fig. 3. Thermograms of 2-HPMA grafted to PET fibers (a) 3.7 %, (b) 12.5 % and (C) 49.0 %

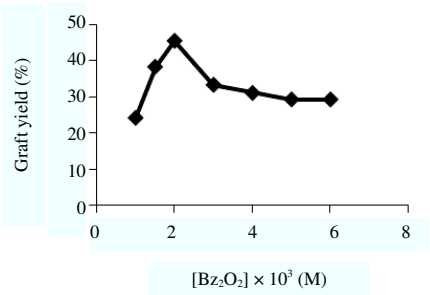


Fig. 4. Effect of Bz_2O_2 concentration on the grafting yield: [2-HPMA] = 0.5 M, temperature = 75 ºC, time = 1 h

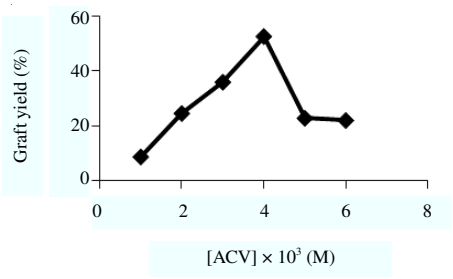


Fig. 5. Effect of ACV concentration on the grafting yield: [2-HPMA] = 0.5, temperature = 75 ºC, time = 1 h

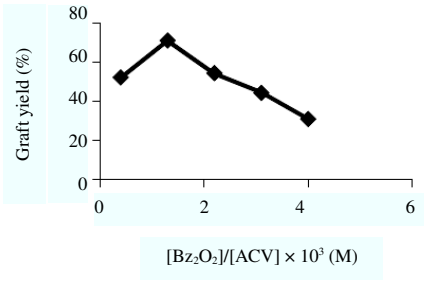


Fig. 6. Effect of mixture of initiators on the grafting yield: [2-HPMA] = 0.5 M, temperature = 75 °C, time = 1 h

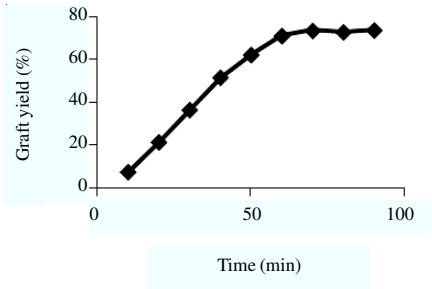


Fig. 7. Effect of time on the grafting yield: $[Bz_2O_2/ACV] = 1 \times 10^{-3}/3 \times 10^{-3}$ M, [2-HPMA] = 0.5 M, temperature = 75 ºC

Dye ability: The results of present study showed that by increasing the percentage of grafted products, their dye ability increases to 21.21 %-grafted product and then it decreases. This fact emphasize the physically absorption of disperse dye onto PET fibers. In fact, when the percentage of grafted yield increase, the number of free sites through which the dye diffuses to the fibers decreases[4,11]. On the other hand, non-ionic emulsifier (OC-30) has showed the greatest effect onto dye ability of the untreated fibers. While CTAB as a cationic emulsifier has not showed any effect onto dye ability. Result are tabulated in Table-1.

TABLE-1
VARIATION OF DYE UPTAKE WITH THE PER CENT OF GRAFTING YIELD

Grafting yield (%)	0.00	14.81	21.21	48.41
Dye/fiber (mg/g)	0.88	1.17	1.56	1.08
Dye/fiber (mg/g) in the presence of 0.5 % SLS	0.55	0.58	0.69	0.81
Dye/fiber (mg/g) in the presence of 0.5 % CTAB	0.08	0.18	0.36	0.45
Dye/fiber (mg/g) in the presence of 0.5 % OC-30	1.05	0.67	0.54	0.40

Conclusion

The effect of 0.5 % non-ionic (OC-30), anionic (SLS) and cationic (CTAB) emulsifiers onto dye ability of disperse dye in ungrafted PET fibers showed the results as follows: OC-30 > without emulsifier > SLS > CTAB and in grafted PET fibers: without emulsifier > SLS > OC-30 > CTAB. On the other hand the absorption of disperse dye onto PET chains showed a decreasing after 21.21 % of graft yield and this fact emphasized the physically absorption of dye onto PET. The use of mixture of initiators (ACV-Bz_2O_2) showed a synergistic effect in grafting yield and the time of reaction decreased. Characterization by FTIR, TGA and SEM confirmed the grafting of 2-HPMA onto PET fibers.

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ERRATUM

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Bioreduction of a Drug Intermediate in Presence of Hexane and Surfactants

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